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RAPID COOLING METHOD FOR PARTS BY CONVECTIVE AND  
RADIATIVE TRANSFER

The present invention relates in general to the  
5 heat treatment of metals and more particularly to the  
operation of gas hardening of steel parts having  
previously undergone heat treatment (such as heating  
before quench, annealing, tempering) or thermochemical  
treatment (such as case hardening, carbonitriding).  
10 Such gas hardening operations are generally carried out  
by circulating a pressurized gas in a closed circuit  
between a charge and a cooling circuit. For practical  
reasons, gas quench hardening installations generally  
operate under pressures between 4 and 20 times the  
15 atmospheric pressure (4 to 20 bar or 4 000 to 20 000  
hectopascals). In the present description, the  
pressure is designated by the bar, with the  
understanding that 1 bar is equal to 1 000 hPa.

Figure 1 very schematically shows an example of  
20 a gas quench hardening installation. This installation  
1 contains a charge 2 to be cooled disposed in a sealed  
vessel 3. The charge is typically surrounded by baffle  
plates 4 to guide the gas flow. A desired gas mixture  
is introduced under pressure at a gas inlet 5, with the  
25 understanding that the cooling gases can, for example,  
be introduced in the form of a preformed mixture or  
that a plurality of distinct gas inlets can be provided  
for introducing various cooling gases separately. A  
connection for placing the vessel under vacuum (not  
30 shown) is routinely provided. A turbine 6 driven by a  
motor 7 is used to circulate the gases, for example by  
passing from a cooling circuit 9 to the charge to be  
cooled 2. The cooling circuit 9 routinely consists of  
pipes conveying a cooling fluid.

35 The installation in figure 1 is only shown by  
way of example of one of the numerous possible and  
existing structures for circulating a cooling gas in a  
vessel. Conventionally, the pressure is about 4 to 20

bar during the cooling phase. Numerous variants are possible, as regards the disposition of the charge, the gas flow direction, and the method for circulating these gases.

5           For practical reasons, the gas most commonly used for cooling is nitrogen, because it is an inert and inexpensive gas. Furthermore, its density is ideal for simple installations with blowers or turbines, and its heat transfer coefficient is sufficiently  
10 satisfactory. In fact, it is known, in gas hardening systems, that the temperature must be lowered as rapidly as possible for the steel transformation to occur satisfactorily, from the austenitic phase to the martensitic phase without passing through the pearlitic  
15 and/or bainitic phases.

          However, it has been observed that in certain critical cases, nitrogen quench hardening installations are not suitable for obtaining a sufficient temperature lowering rate. Hydrogen and helium quench hardening  
20 have therefore been tested. A drawback of the use of these gases is that existing installations, dimensioned for nitrogen quench hardening, particularly as regards ventilation capacity, are not optimized for the use of a gas of substantially different density. Furthermore,  
25 helium is a substantially more costly gas than nitrogen, while hydrogen incurs risks of inflammability and its use requires special precautions.

          It should also be emphasized that all these prior approaches (like those recommending the use of  
30 hydrogen or helium) were based on an attempt to improve only the convective heat transfer in the treatment chamber.

          The prior art can be illustrated by citing the specific approach of patent EP-1 050 592, which  
35 provides for the presence of gases such as CO<sub>2</sub> and NH<sub>3</sub> in the quenching gas, but without any additional improvement in the quenching efficiency in comparison with the inert mixtures already employed, the usefulness of their presence deriving chiefly,

according to the patent, from two factors, on the one hand, the simultaneous achievement of thermochemical effects (oxidation, nitriding, etc.) which can be expected, and, on the other, the easier physical  
5 integration in a comprehensive heat treatment method (e.g. in a case hardening method) because the downstream hardening can then use the same gases as the actual treatment located upstream.

Still in connection with CO<sub>2</sub>, reference can be  
10 made to the following two patents in which, when CO<sub>2</sub> is mentioned in hardening operations, this occurs in a completely different application (for example, in plastics technology as in patent WO 00/07790 or in liquid form as in patent WO 97/15420).

15 In this context, one of the objects of the present invention is to provide a quench hardening installation using a cooling gas that is thermally more efficient than nitrogen but is inexpensive and simple to use, allowing the cooling of the most demanding  
20 materials.

A further object of the present invention is to provide a cooling method using a gas compatible with existing installations currently functioning with nitrogen (and hence not requiring any significant  
25 change to the installation).

To achieve these objectives, the present invention, in a method for rapidly cooling metal parts using a pressurized cooling gas, provides for the use of a cooling gas which comprises one or a plurality of  
30 gases absorbing infrared radiation, selected so as to improve the heat transfer to the part by combining radiative and convective heat transfer phenomena, and so as to improve the convective heat transfer coefficient in comparison with conventional conditions  
35 of cooling with nitrogen.

The concept of "improvement in comparison with conventional conditions of cooling with nitrogen" should be understood according to the invention as

comparing identical pressure, temperature or quenching installation conditions.

The method according to the invention can further adopt one or a plurality of the following technical features:

- the cooling gas also comprises an additive gas selected from helium, hydrogen or mixtures thereof;

- the cooling gas further comprises a supplementary gas;

- the composition of the cooling gas is also adjusted so as to obtain an average density of the cooling gas thus produced which is approximately the same as that of nitrogen;

- the composition of the cooling gas is also adjusted so as to optimize the convective heat transfer coefficient in comparison with the convective heat transfer coefficients of each of the components of the cooling gas considered individually;

- the cooling operation is carried out in a vessel in which the parts to be treated are disposed, the vessel being equipped with a gas stirring system, and the composition of the cooling gas is also adjusted so as to obtain an average density of the cooling gas thus produced which is adapted to said stirring system of the vessel, without the need to make significant changes to said vessel;

- the composition of the cooling gas is also adjusted so that, during the parts cooling phase, endothermic chemical reactions can occur between the absorbent gas or one of the absorbent gases and another of the components of the cooling gas;

- said infrared absorbing gas is  $\text{CO}_2$ ;

- said infrared absorbing gas is selected from the group formed of saturated or unsaturated hydrocarbons,  $\text{CO}$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}_2$ , and mixtures thereof;

- the proportion of absorbent gas in the cooling gas is between 5 and 100%, and preferably between 20 and 80%;

- the cooling gas is a binary CO<sub>2</sub>/He mixture, of which the CO<sub>2</sub> content is between 30 and 80%;

- the cooling gas is a binary CO<sub>2</sub>/H<sub>2</sub> mixture, of which the CO<sub>2</sub> content is between 30 and 60%;

5           - an operation of recycling of the cooling gas is carried out after use, suitable for recompressing the gas before a subsequent use, and, as required, also for separating and/or purifying it, thereby to recover all or part of the components of the cooling  
10 gas.

The invention further relates to the use, in an installation for rapidly cooling metal parts using a pressurized cooling gas, which installation is optimized for operation with nitrogen, of a cooling gas  
15 comprising from 20 to 80% of an infrared absorbing gas and from 80 to 20% of hydrogen or helium or mixtures thereof, the composition of the cooling gas being adjusted so as to make significant changes to the installation unnecessary.

20           As will have been understood, the concepts according to the invention of "choice" of the absorbent gas or gases, or of "adjustment" to obtain the desired properties of heat transfer coefficient, or of density or of endothermic character, must be understood as  
25 pertaining to the nature of the components of the mixture and/or their content in this mixture.

The merit of the present invention is accordingly to stand apart from the conventional approach of the prior art of simply improving the  
30 convective heat transfer conditions, by demonstrating that the proportion of radiative heat transfer in the total heat transfer is between about 7 and 10% (in the range from 400 to 1050°C), hence very significant, and that it is therefore extremely advantageous to address  
35 this aspect of the heat transfer to account for it and to exploit it.

These objects, features and advantages, and others of the present invention, are described in detail in the following non-limiting description of

particular embodiments, provided with reference to the figures appended hereto among which:

- figure 1, previously described, shows an example of a gas quench hardening installation;

5       - figures 2A and 2B show the convective heat transfer coefficient of various gas mixtures at various pressures, in the case of a fluid in parallel flow between cylinders; and

10       - figure 3 shows the variation in temperature as a function of time for various quenching gases used in the same conditions.

According to the present invention, it is proposed to use, as a quenching gas, a gas absorbing infrared radiation or a mixture based on such infrared  
15   absorbing gases (designated below by absorbent gas), such as carbon dioxide ( $\text{CO}_2$ ) and, if required, containing one of more gases having a good convective heat transfer capability (designated below by additive gas) added to it, such as helium or hydrogen.

20       Such a mixture offers the advantage, in comparison with conventional quenching gases or gas mixtures using gases transparent to infrared radiation, such as nitrogen, hydrogen and helium, of absorbing heat both by convective and radiative phenomena,  
25   thereby increasing the total heat flux extracted from a charge to be cooled.

It is possible to add, to this mixture, other gases, designated herein after by supplementary gas, such as nitrogen, considered both as a simple carrier  
30   gas and in a more active role making it possible, as shown below, to optimize the properties of the gas mixture, such as density, thermal conductivity, viscosity, etc.

According to an embodiment of the present  
35   invention, as shown in figures 2A and 2B, it is proposed to use certain gas mixtures as defined above, which further present better convective heat transfer coefficients (kH) in watts per square meter and per Kelvin than each of the gases considered individually.

As shown above in fact, according to one advantageous embodiment of the invention, the composition of the cooling gas is adjusted so as to "optimize" the convective heat transfer coefficient in comparison with  
5 the convective heat transfer coefficients of each of the components of the cooling gas considered individually. The term "optimization" used here should be understood accordingly as taking place at the peak of the curve concerned, or much lower (for example, for  
10 economic reasons) but in any case so as to have a convective heat transfer coefficient that is better than each of the convective heat transfer coefficients of each of the components of the cooling gas considered individually.

15 According to a further advantageous embodiment of the present invention, it is proposed to use an absorbent gas mixture (and if applicable an additive gas) possibly with the addition of supplementary gases, in density conditions optimized so that hardening can  
20 be carried out in quench hardening installations normally designed and optimized to operate in the presence of nitrogen. For this purpose, carbon dioxide is mixed, for example, with helium, used as an additive gas, so as to combine an optimization of the convective  
25 heat transfer coefficient with an average mixture density that is approximately the same as that of nitrogen. Existing installations can accordingly be used with comparable ventilation rates and capacities and existing gas ventilation and deflection structures,  
30 without having to make significant changes to the installation.

This offers the advantage that, in a given installation, optimized for nitrogen hardening, the user can, in normal conditions, when appropriate to the  
35 materials concerned, use nitrogen as a quenching gas and, only in the specific cases of more demanding materials, i.e. when the specific conditions of the parts or the steels to be treated demand specific treatments, use for example the mixture of carbon

dioxide and helium given as an example, or the mixture of carbon dioxide and hydrogen also exemplified herein.

Obviously, as it will appear clearly to a person skilled in the art, if the invention has been particularly illustrated above using CO<sub>2</sub>, other gases absorbing IR radiation are also usable here without departing at any time from the framework of the present invention, such as saturated or unsaturated hydrocarbons, CO, H<sub>2</sub>O, NH<sub>3</sub>, NO, N<sub>2</sub>O, NO<sub>2</sub>, and mixtures thereof.

Similarly, if particular emphasis has been laid above on an advantageous embodiment of the invention, in which the concentrations of the various gases are adjusted to obtain both good heat transfer efficiency and density conditions approaching nitrogen, in order to avoid having to make any significant changes to the installation, it is possible, without departing from the framework of the present invention, to privilege the optimal heat transfer conditions, even if it means using mixtures of density more distant from that of nitrogen, and accordingly having to make changes to the installation, particularly to the stirring motor (adoption of a motor with a different power rating, or of a speed variator system). This could, for example, be the case for a gas mixture comprising 90% CO<sub>2</sub> and 10% hydrogen, with a density about 40% higher than that of nitrogen.

Figure 2A shows, for pressures 5, 10 and 20 bar, the convective heat transfer coefficient  $kH$  of a mixture of CO<sub>2</sub> and helium, for various proportions of CO<sub>2</sub> in the mixture. Thus, the x-axis shows the ratio of the CO<sub>2</sub> concentration,  $c(\text{CO}_2)$ , to the total concentration of CO<sub>2</sub> and He,  $c(\text{CO}_2/\text{He})$ . It may be observed that the convective heat transfer coefficient reaches a peak at CO<sub>2</sub> concentrations between about 40 and 70%, in this case about 650 W/m<sup>2</sup>/K at 20 bar for a concentration of about 60%. Thus, the mixture not only offers the advantage of having a density close to that of nitrogen, but in addition, of having a higher



convective heat transfer coefficient than that of pure CO<sub>2</sub>.

Figure 2B shows similar curves for mixtures of carbon dioxide (CO<sub>2</sub>) and hydrogen (H<sub>2</sub>). It may be observed that the convective heat transfer coefficient kH reaches a peak at CO<sub>2</sub> concentrations between about 30 to 50%, in this case about 850 W/m<sup>2</sup>/K at 20 bar for a concentration of about 40%. Furthermore, it shows that the convective heat transfer coefficient kH is better for a mixture of carbon dioxide and hydrogen than for a mixture of CO<sub>2</sub> and helium.

A further advantage of the use of such a mixture of carbon dioxide and hydrogen is that, under the usual conditions for quench-hardening steel parts, endothermic chemical reactions occur between the CO<sub>2</sub> and the hydrogen, thereby further accelerating the cooling. Moreover, it is observed that in the presence of CO<sub>2</sub>, the explosion hazard associated with hydrogen is substantially reduced, even if oxygen is inadvertently introduced.

Figure 3 shows the result of calculations simulating the cooling of a steel cylinder by convective heat transfer with various cooling gases in the case of a mixture flowing in parallel to the length of the cylinders (cylinders simulating the case of long parts). Curves are shown for pure nitrogen (N<sub>2</sub>), for a mixture containing 60% CO<sub>2</sub> and 40% helium, for pure hydrogen, and for a mixture containing 40% CO<sub>2</sub> and 60% hydrogen. This latter mixture is observed to yield the best results, that is, the highest cooling rate between 850 and 500°C. For this latter mixture, the hardening rate is improved by about 20% over pure hydrogen and by about 100% over pure nitrogen.

Obviously, as already pointed out above, the present invention is susceptible to a number of variants and modifications which will appear to a person skilled in the art, particularly as regards the choice of the gases, the optimization of the proportions of each gas, with the understanding that,

if desired, ternary mixtures such as  $\text{CO}_2/\text{He}/\text{H}_2$  can be used, and that other gases could be added, called supplementary gases above.